Title: The Passivation of Carbon for Improvement of Air Entrainment in Fly Ash Concrete

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SUMMARY

The most widespread and economically attractive option for utilizing fly ash is in concrete manufacture, where the fly ash serves as a partial replacement for Portland cement [Helmuth, 1987; Malhotra and Mehta, 1996]. In most concrete mixtures, specialty surfactants, or "air entraining admixtures," are added to stabilize sub-millimeter air bubbles, which improve resistance to freeze / thaw cycles [Lea, 1970; Ramachandran, 1995; Rixom and Mailvaganam, 1986; Freeman et al., 1997]. Solid carbon residues, if present in fly ash in high concentration, can adsorb these surfactants and render them unable to fulfill their intended function.

Experimental characterization of a set of over 70 U.S. fly ash samples at Brown has identified four primary factors responsible for the adsorptivity of a given fly ash: (1) the carbon content, or LOI, (2) the specific carbon surface area, m^2/g-carbon, (3) the carbon pore size distribution, and (4) the carbon surface *chemistry*. The work suggests that the nonpolar fraction of the total carbon surface area competes directly with the air / water interface for the nonpolar portions of amphiphilic molecules in air entraining admixtures. The ultimate outcome of this competition determines the number and size of air bubbles, and is strongly influenced by the amount of accessible, nonpolar carbon surface area.

The effect of surface chemistry can be directly seen by controlled low-temperature oxidation experiments. Air oxidation reduces the foam index, even at temperatures below which significant carbon consumption occurs [Hachmann et al., 1998]. Oxygen chemisorption is widely accepted as the first step in carbon oxidation [Laine et al., 1963, Lizzio et al., 190] and the formation of a significant stable oxide layer has been observed in the early stages of low temperature oxidation [Lizzio et al., 1988, Floess et al., 1988]. In our data, initial oxygen chemisorption occurs in the temperature range 300 - 450 ^{o}C in air prior to significant weight loss, leading to an increase in surface polarity and corresponding decreases in specific surfactant adsorptivity. This conclusion is consistent with the prior observation of the effect of surface oxidation on carbon black surfactant adsorptivity [Gao et al., 1997]. The oxidative surface treatment of carbon shows promise as an economic ash beneficiation process if it could be conducted at lower temperatures.

The Effect of Ozone

Recent work demonstrates a room temperature process for passiviation of carbon based on ozone. Dry ozonation dramatically reduces the foam index of a carbon-containing ash while producing slight increases in the loss-on-ignition value — i.e. it does not remove carbon by full oxidation, but rather introduces oxygenated surface groups that slightly increase the sample weight. (This chemisorbed oxyen is removed by heating to 700 ^{o}C in the LOI test, thus yielding very slight increases in LOI.).

A very large set of laboratory ozonation experiments has been conducted using a variety of ash samples, admixtures, contact times, and ozone concentrations. The results indicate that ozone is remarkably effective at reducing or eliminating the surfactant adsorptivity of carbon at typical addition rates of 0.5 - 3 gm-O_3/kg ash processed. Preliminary economic analysis suggests that this amount of ozone can be generated in an economic fashion, with electricity costs for ozone generation on the order of 1 $ / ton ash. Work is underway with several industry partners to assess the commercial potential of large-scale ash ozonation. At this stage, we can identify the following potential advantages and disadvantages of this reactive treatment process:

Potential Advantages of Ozonation

- simple in concept and operation
- low operating costs, consisting primarily of electricity
- large-scale ozone generation is proven, off-the-shelf technology applied in water treatment, bleaching operations, and food processing.
- allows control over ash properties by varying ozone usage
- does not generate a high-carbon waste stream (as do separation processes).
- might be carried out in existing ash handling equipment

Potential Disadvantages of Ozonation

- ozone is toxic and must be handled in sealed units.
- process leaves carbon in place, thus leaving regulatory hurdles based on LOI in some cases.

In our data, ash samples with LOI as high as 33% have been successfully ozonated to yield low surfactant activities — we currently believe there is no fundamental limit to the extent of deactivation by ozone. In the future, therefore, many ash streams may become good candidates for ozonation, in particular ashes that meet the ASTM specifications (up to 6% carbon, or up to 12 % carbon with air entrainment testing) but behave poorly in the field if used without treatment. In the immediate future, however, several real utility cases involving problem ashes with LOI near 1% may provide an ideal entry point for the initial demonstration of this new technology.

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